

**Electronic Structure of
Impurities and Vortices in
Short Coherence Length Superconductors**

Annual Report

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PROGRAM GOALS

This grant is for a twenty-seven month investigation of the influence of impurities and vortices on the nearby electronic structure in a short coherence length superconductor. The primary goal is to develop self-consistent calculations of the electronic structure near various defects, focusing on the local density of states (LDOS) measurable by an STM. These calculations are to be compared with analytic results in various limits. Pairing functions of *d*-wave and *s*-wave symmetry are to be considered. Results for the local electronic structure are expected to be of great utility in understanding macroscopic measurements such as planar tunneling spectra, critical currents and the magnetic penetration depth, but the application of theoretical results to these problems is currently not funded.

PROGRESS

In this, the second year of this grant, we have applied a powerful Green's function technique for finding the local electronic structure near impurities to high-temperature superconductors. This technique was developed during the first year of this grant and initially applied to isotropic-gap low-temperature superconductors. The application in this year was to *d*-wave and extended *s*-wave superconducting gaps in quasi-two-dimensional high-temperature superconductors, particularly $\text{YBa}_2\text{Cu}_3\text{O}_7$ (YBCO). These calculations include self-consistent determinations of the order parameter, and a reasonable model of the normal-state band structure. The calculations have essentially arbitrary energy resolution throughout the spectrum.

The most striking result from these investigations was a fit to experimental *planar* tunneling spectra from three different groups on YBCO. None of these spectra look like a clean *d*-wave superconductor's density of states.

Nevertheless all four tunneling curves examined were fit by adding nonmagnetic impurities of essentially the *same scattering strength* to a *d*-wave superconductor in different concentrations and assuming slightly different voltage resolutions. We believe that these impurities, which are present in concentrations on the order of 1% even in nominally clean samples, are oxygen vacancies near the surface of YBCO. These results are also supported by scanning tunneling spectroscopy (STS) on the YBCO surface.

In addition to these striking results, several properties of the impurity-associated resonances were investigated systematically. The energies of resonance impurity-assicated states in superconductors with anisotropic gaps were determined, and their lineshapes were evaluated and found to be highly asymmetric. Furthermore it was determined that any anisotropic order parameter would have associated with it two resonances, regardless of order parameter symmetry. Thus it is important to measure the energies of these resonances to determine the order parameter symmetry accurately. The suppression of the gap-edge features in the spectra was calculated for the first time, and the local changes in the order parameter were determined.

LIST OF ATTACHED PAPERS

1. Michael E. Flatté and Jeff M. Byers, "Impurity effects on quasiparticle c-axis tunneling and STM spectra in high-T_c cuprates", *Physical Review Letters* **80**, 4546-4549 (1998). Application of the Koster-Slater technique to anisotropic-gap superconductors, including *d*-wave and extended *s*-wave gaps in YBa₂Cu₃O₇.

INVITED PAPERS

1. Michael E. Flatté and Jeff M. Byers, "Local Electronic Structure of Defects in Superconductors", a chapter in *Solid State Physics, Volume 52*, Academic Press, New York, 1998. Extended summary of work performed under this grant and prior to it on local properties of impurities in superconductors.

INVITED TALKS

1. Michael E. Flatté, "Local electronic properties of defects in superconductors", 1998 March Meeting of the American Physical Society, Los Angeles, March 16-20, 1998.
2. Michael E. Flatté, "Local electronic properties of defects in superconductors", Solid State Seminar, U. Pittsburgh, April 23, 1998.

Impurity Effects on Quasiparticle *c*-Axis Planar Tunneling and STM Spectra in High-*T_c* Cuprates

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We present self-consistent calculations of the electronic structure near strongly scattering impurities in cuprate superconductors described by a realistic band structure and order parameter magnitude. Energies and highly asymmetric line shapes of resonances, changes in gap-edge features, and local changes in the order parameter are determined for magnetic and nonmagnetic potentials. Experimental tunneling spectra are well fitted by calculations using a *d*-wave order parameter. The local density of states near such impurities is also calculated. [S0031-9007(98)06003-7]

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Planar tunneling provided a key tool for exploring the character of the superconducting state in low-temperature superconductors such as lead [1], and several measurements have been made in the high-temperature superconductors, principally on YBa₂Cu₃O_{7-δ} (YBCO) [2–4]. These measurements indicate (on YBCO) a greater density of states within the gap than consistent with the simple *d*-wave order parameter expected from angle-resolved photoemission spectroscopy [5] and Josephson π -junction [6] experiments. Theoretical examination of *d*-wave superconductors has shown that impurities can provide spectral weight within the gap, even at the chemical potential. Unfortunately calculations of resonant state effects in *c*-axis tunneling [7–9] which have the spectral resolution to resolve the resonances in energy [10] are quite limited. The band structures used were particle-hole symmetric with circular Fermi surfaces, order parameter self-consistency was ignored, and calculations were limited to resonances with energies $\Omega \ll \Delta_{\max}$, where Δ_{\max} is the order parameter maximum on the (normal) Fermi surface. The importance of a correct band structure has been established in recent calculations of *T_c* suppression [11] and photoemission spectral weights [12]. Furthermore in *c*-axis tunneling calculations only the effects of impurities on resonances were considered; the effects on features elsewhere in the spectrum, such as the gap edge, were ignored.

A complementary probe to planar tunneling is scanning tunneling spectroscopy (STS), which is best suited for exploring local properties at the surface of a sample. The *local* structure of impurities in superconductors with anisotropic order parameters has been the topic of increased investigation since two almost simultaneous events: the calculation of anisotropic structure in the local density of states (LDOS) around an impurity indicative of the order parameter symmetry and structure of the host superconductor [13], and the demonstration of the sensitivity of STS to the propagation properties of the host material around an impurity atom [14]. Recent work [15,16] has evaluated exactly the mean-field spa-

tial structure of localized states [17–19] around classical (static, or elastic) magnetic impurities in superconductors with order parameters which are *isotropic* in the absence of impurities; this type of order parameter will be referred to as *s* wave. Such systems have recently been explored experimentally with STS [20]. Calculations in Refs. [15,16] are based on a Koster-Slater technique for finding the real-space Green's functions (and thus the LDOS). The submillivolt sub-Angstrom resolution of STS makes it the best tool for probing properties of an isolated impurity, and justifies the effort to calculate these local properties.

We present here the first calculations of *c*-axis planar tunneling spectra and local STS spectra on YBCO which use a correctly particle-hole asymmetric band structure, include a self-consistent determination of the order parameter, and produce spectra with essentially arbitrary energy resolution throughout the spectrum. The resonances are characterized by extremely asymmetric line shapes. We find, in contrast to previous work [8], that there are at least two resonances or localized states for a given magnetic potential or a given nonmagnetic potential for all anisotropic order parameters [21]. Hence the presence of a resonance around a nonmagnetic impurity is not *per se* an indication of a particular order parameter symmetry. We also calculate the ground state spin and order parameter as a function of impurity strength for several order parameters.

We further fit the (quite varied) planar tunneling results of three different experimental groups (shown in Fig. 1). None of the curves in Fig. 1 look like a typical clean *d*-wave superconductor's DOS. Nevertheless all four curves are fit by adding impurities of essentially the same scattering strength to a *d*-wave superconductor in different concentrations and assuming slightly different voltage resolutions. The experimental drop in differential conductance due to the gap structure is only about 30%; we interpret the large residual differential conductance as due to a metallic background originating from the copper-oxygen chains [22]. Note that these results are

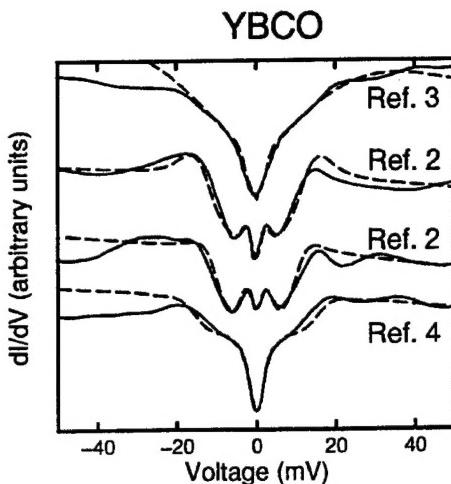


FIG. 1. Comparison of theoretical results (dashed lines) with measurements (solid lines) from Refs. [2–4]. The impurity parameters used were, from top down, $V_0 = 2t$, $n_i = 1.7\%$; $V_0 = 2.5t$, $n_i = 0.5\%$; $V_0 = 2.5t$, $n_i = 1.1\%$; and $V_0 = 2t$, $n_i = 1.4\%$.

also consistent with magnetic impurities in an s^* -wave superconductor at roughly double the concentration (the s^* -wave order parameter has the same magnitude as the d -wave one, but does not change sign). We believe that these impurities, which are present in concentrations on the order of 1% even in nominally clean samples, are oxygen vacancies near the surface of YBCO.

This view is supported by STS on the YBCO surface [22]. Our calculations of the LDOS at the impurity site agree with STS measurements [22] near oxygen vacancies on the YBCO surface. The LDOS is shown in Fig. 2 for magnetic and nonmagnetic impurities in a d -wave superconductor at sites near the impurity along the (10) direction and also along the (11) direction. Also shown is the measured LDOS at an oxygen vacancy [22]. At the impurity site there is no evidence of the gap features, and the spectrum is dominated by an asymmetric resonance. Immediately adjacent to the impurity the gap-edge feature begins to recover in strength. Whereas the DOS for potentials of $2.5t$ and $10t$ are roughly identical, and thus the results in Fig. 1 can be fitted with either potential strength, the LDOS at the impurity site is entirely holelike for $2.5t$ and electronlike for $10t$, where $t = 350$ meV is the nearest-neighbor hopping element for the band structure (described below). Since the measured LDOS at the oxygen vacancy is holelike, the potential strength of the oxygen vacancy must be $2-2.5t$. Although our surface model is incomplete (e.g., it does not include the copper-oxygen chains), supporting evidence is provided by STS [22] identification of a broad resonance at the oxygen vacancies for positive sample bias voltages around 700 meV, consistent with a potential of $2.5t$. We regard Figs. 1 and 2 as the principal results of this Letter.

The LDOS and DOS are calculated using an inversion procedure based on the Gor'kov equation. This procedure is similar to one used to calculate the local electronic

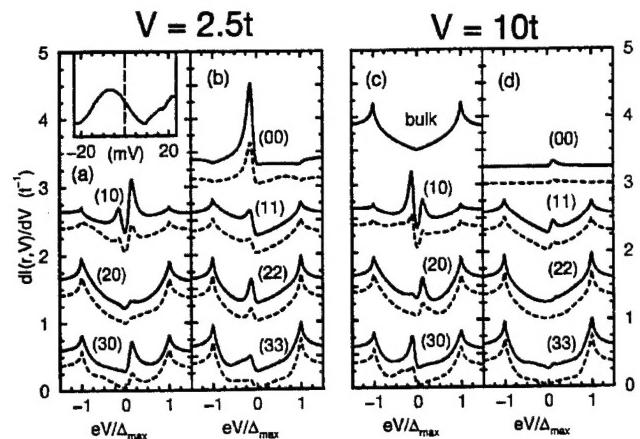


FIG. 2. Local differential conductance $[dI(r, V)/dV]$, relative to the normal metal for potentials of [(a) and (b)] $2.5t$ and [(c) and (d)] $10t$, shown as a function of the voltage. The series of curves are for different distances (sites on the square lattice) from the impurity. The solid lines are for nonmagnetic potentials and the dashed lines are for magnetic potentials. (a) and (c) show from one to three lattice spacings along the (10) direction from the impurity while (b) and (d) show from the origin to three lattice spacings along the (11) direction on the square lattice. An inset to (a) shows the measured STS spectrum on an oxygen vacancy (Ref. [22]). Also shown in (c) is the homogeneous (clean) tunneling spectrum.

structure near defects in isotropic s -wave superconductors [15,16]. The advantages of this technique over the alternative of finite-size diagonalization include (i) the Gor'kov equation for a static impurity is diagonal in frequency, so arbitrary frequency resolution is possible, (ii) the range of the inhomogeneous potential determines the numerical difficulty of calculating the spectra, and (iii) self-consistent potentials, such as the above order parameter variation or an on-site Coulomb repulsion, are easy to implement [23]. More details will be available in a forthcoming publication [24].

The Hamiltonian considered,

$$H = \sum_{(ij),\sigma} [-t_{ij}c_{i\sigma}^\dagger c_{j\sigma} + \Delta_{ij}c_{i\uparrow}^\dagger c_{j\downarrow} + \Delta_{ij}^*c_{j\downarrow}^\dagger c_{i\uparrow}] + V_S(c_{0\uparrow}^\dagger c_{0\uparrow} - c_{0\downarrow}^\dagger c_{0\downarrow}) + V_0(c_{0\uparrow}^\dagger c_{0\uparrow} + c_{0\downarrow}^\dagger c_{0\downarrow}), \quad (1)$$

includes a single-site potential which can be magnetic (V_S), nonmagnetic (V_0), or a combination of both. The homogeneous electronic structure has nearest- and next-nearest-neighbor hopping elements of $t = 350$ meV and $t' = -56$ meV, respectively, and a filling of 1.13. Only on-site and nearest-neighbor Δ_{ij} are nonzero, and $\Delta_{\max} = 25$ meV.

The numerical results presented in this Letter are obtained by inverting the Gor'kov equation, $\mathbf{G} = \mathbf{g} + \mathbf{g}\mathbf{VG}$, for this Hamiltonian within a real-space region around the impurity beyond which the potential is negligible. Since the nonmagnetic and magnetic potentials are localized to a

single site, the only potential which is ignored outside this square is the off-diagonal potential (in the Nambu formalism) due to the local change in the order parameter. The Δ_{ij} 's are found self-consistently in the inversion process for the Gor'kov equation. Spectra outside this real-space region (typically a square 20 lattice spacings on a side) are constructed according to the generalized T-matrix equation: $\mathbf{G} = \mathbf{g} + \mathbf{g}\mathbf{V}[\mathbf{I} - \mathbf{G}\mathbf{V}]^{-1}\mathbf{g}$. The energy resolution of the calculations is $\Gamma = 0.35$ meV, and all spectral features presented here are much wider than Γ . Once \mathbf{G} has been calculated throughout the region near the impurity, the LDOS, $A(i; \omega) = \sum_{\sigma}(-1/\pi)\text{Im}G_{\sigma}(i, i; \omega)$, is straightforward to evaluate. Furthermore the DOS is obtained by spatially integrating the LDOS. The calculated energies of the resonances, identified by peaks in the DOS, are shown for nonmagnetic potentials in Fig. 3.

To obtain an analytic result with which to compare

$$R(\alpha, \beta, v_s, v_0) = \frac{v_s \pm \sqrt{v_s^2 - (1 - \beta)(v_s^2 - v_0^2)[1 - 2v_0\alpha - (v_s^2 - v_0^2)(\beta + \alpha)]}}{(1 - \beta)(v_s^2 - v_0^2)}. \quad (3)$$

Since $\Omega < \Delta_{\max}$ when R is finite, which it is for all *anisotropic* order parameters ($\beta < 1$), there always are two solutions to Eqs. (2) and (3) for anisotropic order parameters [21]. For the nonmagnetic case ($R = \sqrt{[(1 - \alpha v_0)^2 + \beta v_0^2]/(1 - \beta)v_0^2}$) resonances come in pairs due to the spin degree of freedom.

Resonance energies from the above expressions are shown in Fig. 3. The particle-hole asymmetry is due to the nonzero α ; for $\alpha = 0$ the resonance energies are identical for $\pm v_s$. The main source of disagreement comes from the use of a standard method of finding resonances: solving for the zeros of the real part of the T-matrix denominator. This strategy is flawed for this

we find the zeros of the real part of the denominator of an approximate T matrix. The electronic structure of the homogeneous superconductor is parametrized with two frequency-independent parameters. The first, α , was introduced in Ref. [15] for *s*-wave superconductors, and parametrizes the particle-hole asymmetry of the band structure. The second, β , is approximately the square of the ratio of the root mean square average of the order parameter around the Fermi surface to its maximum value (Δ_{\max}). $\beta = 1$ for *s* wave, and $\beta = 0$ for *d* wave. Order parameter variation due to the impurity potential is ignored. Defining dimensionless quantities $v_s = \pi N_0 V_s$ and $v_0 = \pi N_0 V_0$ [where N_0 is the density of states at the (normal) Fermi surface] we find resonances for the energies

$$\Omega = \left(\frac{R^2(\alpha, \beta, v_s, v_0)}{1 + R^2(\alpha, \beta, v_s, v_0)} \right)^{1/2} \Delta_{\max}, \quad (2)$$

where

system due to the strongly energy-dependent imaginary component of the T-matrix denominator.

In contrast to the resonances for the *d*-wave system, resonances for nonmagnetic impurities in an *s*^{*}-wave system do not have lower energy than $\Omega = 0.77\Delta_{\max}$. Hence if the order parameter were *s*^{*} wave, in order to produce the results of Figs. 1 and 2, oxygen vacancies would have to behave as *magnetic* impurities.

The difference spectra for nonmagnetic and magnetic impurities in *d*-wave and *s*^{*}-wave superconductors are shown in Fig. 4. A difference spectrum is the change in the DOS due to the addition of one impurity. Shown are the reductions in the density of states near the gap feature, present even in the absence of resonances [Fig. 4(d)]. Spectral weight pulled to lower energies in the presence of the impurity exactly compensates for that taken from the gap feature. A resonance's line shape is much sharper on the low-energy side and broader on the high-energy side, due to the frequency-dependent DOS in the homogeneous superconductor. This also shifts the energy of the peak of a resonance.

Figure 5(a) shows for magnetic impurities the order parameter at the impurity, and in the inset [25] the total spin of the superconductor's ground state. In contrast to the isotropic *s*-wave case, where the order parameter at the impurity changes abruptly at some critical potential strength [15], for *d* wave the order parameter changes smoothly at all potentials, due to the finite width of the resonant state. For *s* wave this transition is characterized by the binding of a quasiparticle in the ground state [9,15,19], producing an abrupt change in the ground-state spin of the superconductor from 0 to 1/2. For the *d*-wave superconductor there is instead a cloud of quasiparticles near the impurity potential. The nonquantized behavior arises because there are quasiparticle states at the chemical

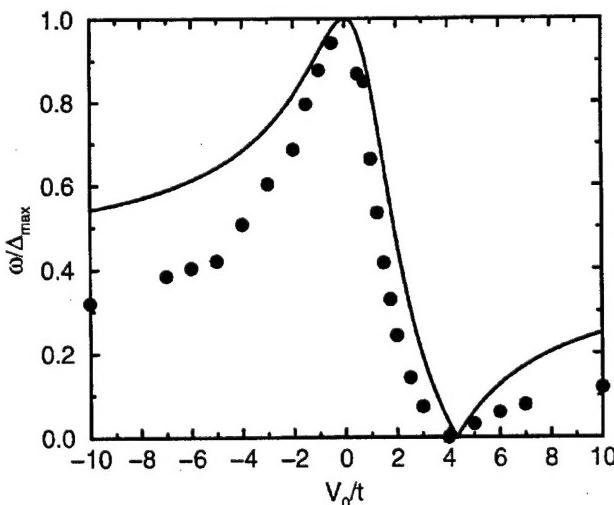


FIG. 3. Peak energies of resonant states created by a nonmagnetic impurity. Shown are the calculated results for a *d*-wave superconductor (circles) and an analytic model which includes particle-hole asymmetry [Eqs. (2) and (3)].

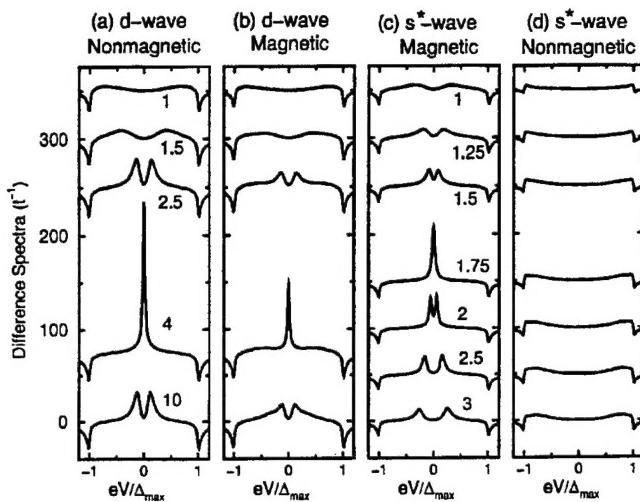


FIG. 4. Difference spectra (in units of t^{-1}) for (a) nonmagnetic and (b) magnetic impurities in a *d*-wave and (c) magnetic impurities and (d) nonmagnetic impurities in an *s**-wave superconductor. The numbers are the potential strengths in units of t , and are the same in (a) and (b), as well as for (c) and (d).

potential in the *d*-wave superconductor, but not in the *s*-wave superconductor.

The *d*-wave order parameter changes sign for sufficiently strong positive (electron repelling) nonmagnetic impurities [shown in Fig. 5(b)], but not for magnetic impurities or negative nonmagnetic impurities. The difference between positive and negative nonmagnetic impurities is due to the holelike character of the Fermi surface—a nonmagnetic potential which repels electrons attracts the holes to the impurity. The positive nonmagnetic impurity attracts twice as much hole weight (due to spin degeneracy) to the impurity as the magnetic impurity, so the order parameter suppression is greater. A change in the order parameter sign may affect the presence or absence of a Josephson π junction [26], should the coupling across an interface be near nonmagnetic impurities, such as in a rough junction.

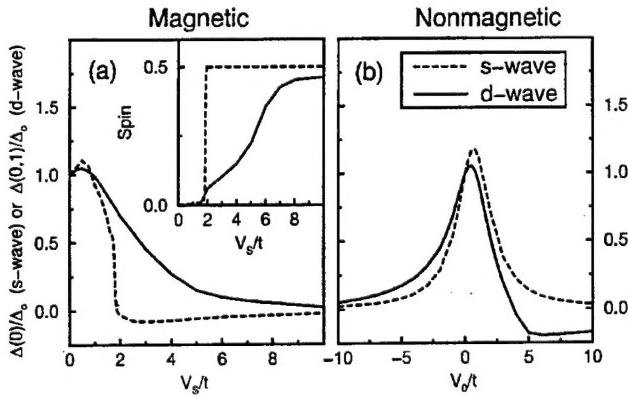


FIG. 5. Change in the order parameter at the impurity for (a) magnetic potentials, and (b) nonmagnetic potentials. Inset in (a) is the ground-state spin for magnetic potentials.

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13. ABSTRACT (<i>Maximum 200 words</i>) This is a report of progress in theoretical calculations of scanning tunneling microscopy spectra near impurities in superconductors. A previously-developed Green's function technique is applied to superconductors with anisotropic gaps, such as d-wave or extended s-wave. Calculations of planar tunneling spectra can reproduce the quite different results from several different groups with a d-wave gap and a small amount (1%) of impurities. These impurities are believed to be oxygen vacancies. A systematic investigation of the properties of impurity-associated resonance states in the gap has also been done.		
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